



Coulometric Study of Acetate Adsorption at a Polycrystalline Platinum Electrode

by Sol Gilman

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Sensors and Electron Devices Directorate, ARL

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Contents

List of Figures	iv
List of Tables	iv
Acknowledgments	v
1. Introduction	1
2. Experimental	1
2.1. Supplies and Equipment.....	1
2.2. Electrodes	2
2.3 Procedures: Potential Scans.....	2
3. Results and Discussion	3
3.1 Electrolyte Purity.....	3
3.2 Determination of Rates of Adsorption	4
3.3 Determination of Rates of Desorption.....	7
3.4 Oxidation State of Adsorbed Acetate.....	9
3.5 Adsorption Isotherm for Acetate Adsorption.....	9
3.6 Concentration Dependence of Equilibrium Acetate Adsorption.....	11
4. Conclusions	12
5. References	13
List of Symbols, Abbreviations, and Acronyms	14
Distribution List	15

List of Figures

Figure 1. Anodic scans for a Pt electrode in a 1N perchloric acid (HClO_4) solution with/without addition of 10^{-4}M acetic acid at a 0.722-V sweep speed (v) = 1000 V/s.	4
Figure 2. Differential anodic charge corresponding to adsorption of acetate at 0.722 V from a 10^{-4}M solution of acetic acid in 1N HClO_4 ; v = 1000 V/s. The straight line corresponds to diffusion control calculated from equation 2, with n = 4.	5
Figure 3. Differential anodic charge corresponding to adsorption of acetate at various potentials from a 10^{-4}M solution of acetic acid in 1N HClO_4 at short adsorption times, v = 1000 V/s. The straight line corresponds to diffusion control calculated from equation 2, with n = 4.	6
Figure 4. Differential anodic charge corresponding to adsorption of acetate at various potentials from a 10^{-4}M solution of acetic acid in 1N HClO_4	7
Figure 5. Differential anodic charge when desorbing acetate at $U_{\text{des}} = 0.4$ V after 20 s of adsorption at $U_{\text{ads}} = 1.4$ V, using sequence from table 2. Concentration of acetic acid = 10^{-4}M in 1N HClO_4	8
Figure 6. Differential anodic charge when desorbing acetate at $U_{\text{des}} = 0.334$ V after 20 s of adsorption at $U_{\text{ads}} = 0.734$ V, using sequence from table 2. Concentration of acetic acid = 10^{-4}M in 1N HClO_4	9
Figure 7. Fractional surface coverage with acetate for a 10^{-4}M solution of acetic acid in 1N HClO_4 . Values of Θ for potentials of 1.0 V or less are equilibrium values; Θ for potentials greater than 1.0 V show slow increase after 1000 s.	10
Figure 8. Concentration dependence of fractional surface coverage with acetate ions; 1N HClO_4 supporting electrolyte.	12

List of Tables

Table 1. Procedure for obtaining anodic adsorption scans.	3
Table 2. Procedure for obtaining anodic desorption scans.	3

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1. Introduction

The adsorption of acetic acid on platinum is of special interest in connection with the attempt to develop technology for direct ethanol fuel cells. Acetic acid has been identified (1–4) as one of the final products of anodic oxidation of ethanol at a platinum (Pt) electrode, the other products being acetaldehyde and carbon dioxide. Knowledge of the adsorptive behavior of acetic acid may provide some guidance as to how this “dead end” product may be avoided or further oxidized.

Prior investigations of acetic acid adsorption have used mainly radioisotopic and spectroscopic techniques to provide information on the extent of adsorption and the structure of the adlayer. Corrigan et al. (6) used radiotracer and infrared spectroscopy for examination of acetic acid adsorption on polycrystalline Pt foil electrodes from a 0.1M perchloric acid electrolyte. Plots of surface excess were provided for two concentrations of acetic acid after “equilibration” of the electrode following activation by electrochemical cycling. The authors also noted that acetic acid delayed the onset of oxygen adsorption during an anodic scan. Rodes et al. (7), using Fourier transform infrared (FTIR) spectroscopy, concluded that acetic acid in perchloric acid electrolyte adsorbed as the anion on single crystals of Pt. An analysis of potential-step data for a single crystal Pt electrode in a perchloric acid electrolyte led Fakuda and Aramata (8) to conclude that the adsorption involved one-electron oxidation of acetic acid. However, based on their results using attenuated total reflectance (ATR)-FTIR spectroscopy, Heinen et al. (9) concluded that the adsorbed species is an intact acetate ion.

In prior (9, 10) studies of chloride and phosphate ion adsorption, I found that the adsorbed ions blocked the adsorption of oxygen (i.e., surface oxidation) on polycrystalline Pt in a quantitative manner allowing measurement of adsorption rates and of saturation coverages for those ions starting with a freshly activated surface. A similar approach was followed in the present study of acetate adsorption.

2. Experimental

2.1. Supplies and Equipment

All measurements were made at room temperature (21 °C) in a 1N solution of perchloric acid with various additions of ethanol. The acid solution was prepared using “Millipore” water with a resistivity of 18.2 MΩ-cm and redistilled perchloric acid (Sigma-Aldrich). Ethanol was 99.5% American Chemical Society (ACS) reagent grade (Aldrich). The electrolyte solution was purified using a “getter” electrode. The getter electrode was cathodically/anodically cycled several times in electrolyte external to the main test vessel. After the final anodic treatment

(producing a protective passive state), the electrode was transferred to the test vessel, cathodically reduced, and held at 0.4 V for several hours with vigorous bubbling of argon. Electrochemical measurements were made using a Gamry Reference 3000 potentiostat. The test vessel was constructed of Pyrex glass with polytetrafluoroethylene (PTFE) stoppers and a PTFE tube for degassing the solution with reagent grade argon.

2.2. Electrodes

The working electrode was a chemically pure (CP) grade Pt wire of 0.08 cm diameter and 1 cm length. The wire was etched lightly in aqua regia, flame annealed, encased in shrinkable PTFE tubing to expose a 1-cm length, and then lightly etched again. The working electrode was periodically immersed in hot chromic acid cleaning solution. Based on cathodic hydrogen adsorption, the electrode had a roughness factor of 2.1 that remained constant over several months of use. The counter electrode was a platinized Pt foil with a 2-cm² geometric area. The use of a palladium-hydrogen (Pd/H) electrode as reference allowed very close placement parallel to the working electrode. It was prepared in a manner similar to that described by Fleischmann and Hiddlest (*10*): a 0.076-cm-diameter wire of a length of 1 cm was spot-welded to a long Pt wire that was sealed in a shrinkable PTFE tube so as to conceal the weld. The electrode was etched in aqua regia and made cathodic at 24 mA for 17 min (past the point of coulombic stoichiometry for Pd/H) and then anodic for 4.5 min. This electrode was found to be stable for several days with a potential of ~0.02 V versus a reversible hydrogen electrode. The electrode was rehydrogenated after several days of use and its potential was monitored against a saturated calomel electrode (SCE) every few hours. All potentials applied and reported here were adjusted to that of a reversible hydrogen electrode. The “gettering” electrode used for electrolyte purification was a platinized Pt gauze cylinder, 55 mm long and 15 mm in diameter.

2.3 Procedures: Potential Scans

Anodic scans were employed to follow the rates of acetic acid adsorption and desorption after employing a staircase of potentials as outlined in tables 1 and 2.

Table 1. Procedure for obtaining anodic adsorption scans.

Step No.	Potential (V)	Conditions	Purpose
1	0.0	Bubble/stir with argon for 1 s.	Desorb the anionic impurities.
2	1.8	Bubble/stir with argon for 2 s.	Oxidize the adsorbed organics and passivate the surface.
3	0.125	Bubble/stir with argon for 1 s; quiescent for 90 s.	Eliminate the concentration gradients and establish conditions for linear diffusion to a clean, active surface.
4	U_{ads}	Quiescent solution for specified adsorption time	Allow adsorption of acetate to a clean surface under conditions of linear diffusion for a period of a few seconds.
5	0.7 V.(for $U_{\text{ads}} < 0.8\text{V}$)	Quiescent solution, 0.0005 s pulse	Provide the same starting potential for the scans .
6	Anodic scan, at speed v.	Quiescent solution	Record the current-time response.

Table 2. Procedure for obtaining anodic desorption scans.

Step No.	Potential (V)	Conditions	Purpose
1-4		Same as 1-4, table 1	Same as 1-4, table 1
5	U_{des}	Quiescent solution	Desorb the adsorbed acetate for a specified desorption time.
6	0.7	Quiescent solution	Eliminate the concentration gradients and establish conditions for linear diffusion to a clean, active surface.
4	U_{ads}	Quiescent solution for specified adsorption time	Allow adsorption of acetate to a clean surface under conditions of linear diffusion for a period of a few seconds.
5	U_{des}	Quiescent solution for specified desorption time	Allow desorption of acetate adsorbed in the previous step.
6	0.7 (for $U < 0.8$)	Quiescent solution, 0.0005 s pulse	Provide the same starting potential for the scans.
7	Anodic scan, at speed v	Quiescent solution	Record the current-time response.

3. Results and Discussion

3.1 Electrolyte Purity

Trace 1 of figure 1 is representative of the anodic scans at 1000 V/s/ that are obtained for the 1N perchloric acid solutions with no added acetic acid, using the procedure from table 1. For adsorption times of from 0.005 to 10 s, the scans are identically superimposable without electrolyte purification. For longer periods after surface reduction/activation, the use of a

gettering electrode as described previously, provided exact duplication of the anodic scans for upwards of 100 s, with a slight distortion of the traces after 1000 s (the longest adsorption time in this study) if the electrolyte was not stirred.

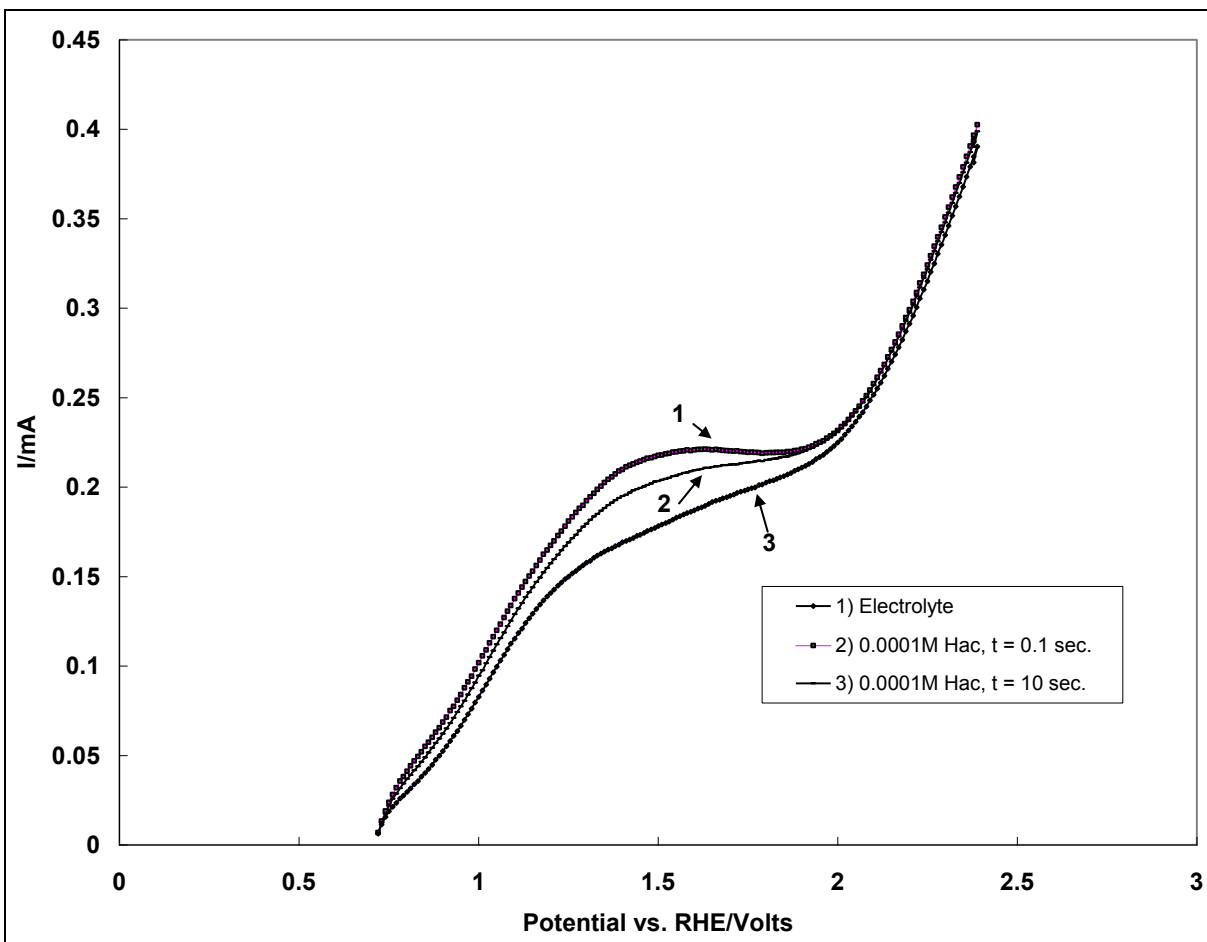


Figure 1. Anodic scans for a Pt electrode in a 1N perchloric acid (HClO_4) solution with/without addition of 10^{-4}M acetic acid at a 0.722-V sweep speed (v) = 1000 V/s.

3.2 Determination of Rates of Adsorption

Figure 1 presents representative traces obtained using the sequence from table 1 with $v = 1000 \text{ V/s}$, $U_{\text{ads}} = 0.722 \text{ V}$, and adsorption times of $t = 0$ (electrolyte only), 0.1, and 10 s. The concentration of acetic acid for the latter two traces was 10^{-4}M . Values of ΔQ were obtained by measuring the closed area between the between the $t = 0$ traces and traces at $t = 0.1$ or $t = 10$ s. ΔQ is the charge corresponding to blockage of oxygen adsorption minus a relatively small charge corresponding to the lowering of the double layer capacitance by the adsorbed acetate. No attempt was made to compensate for resistive distortion to such traces as that would not affect the measured charge. Traces for the same condition of adsorption time and solution concentration were found to be exactly superimposable if the placement of electrodes was not

changed. Reproducibility of traces is essential for the accurate measurement of the relatively small values of ΔQ obtained in this study.

Values of ΔQ for $U_{\text{ads}} = 0.722$ and an acetic acid concentration of 10^{-4}M are plotted against \sqrt{t} in figure 2. For approximately 2/3 of the final value of ΔQ , the relationship between ΔQ and t is linear, suggesting diffusion-controlled adsorption. Semi-infinite linear diffusion can be expected to apply to the diffusion of acetate to our electrode for small values of t (11):

$$I_d = n\pi^{-1/2}FAD^{1/2} Ct^{-1/2}. \quad (1)$$

Integrating equation 1, the corresponding charge is given by equation 2:

$$Q_d = 2n A\pi^{-1/2}FD^{1/2} Ct^{1/2}, \quad (2)$$

where

n = number of equivalents of “oxygen adsorption” electrons blocked by adsorption of one mole of acetate ion

F = Faraday constant

A = area = 0.26 cm^2

D = diffusion coefficient of acetic acid = $1.25 \times 10^{-5}\text{ cm}^2/\text{s}$.

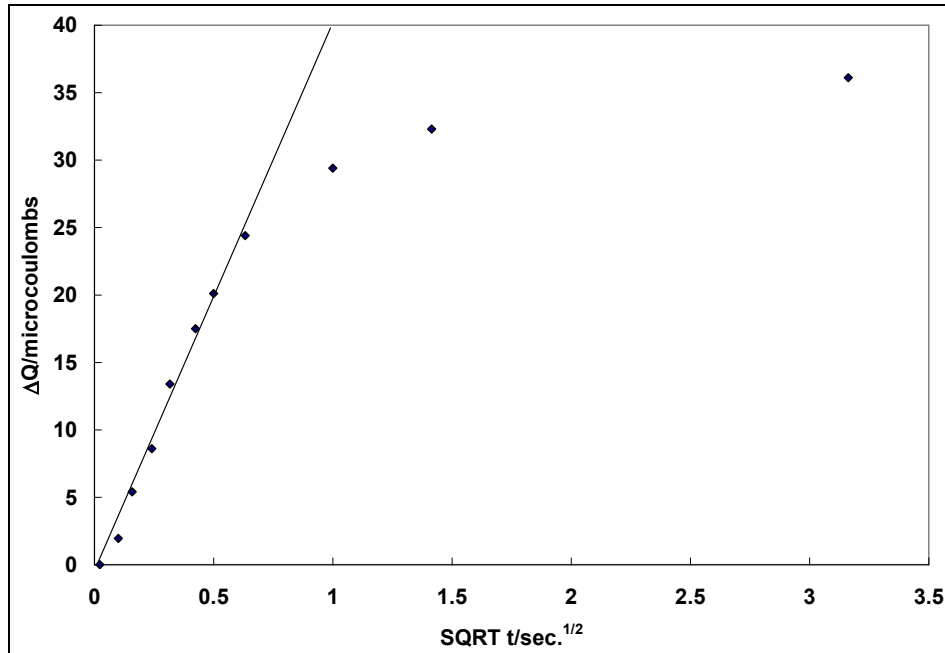


Figure 2. Differential anodic charge corresponding to adsorption of acetate at 0.722 V from a 10^{-4}M solution of acetic acid in 1N HClO_4 ; $v = 1000\text{ V/s}$. The straight line corresponds to diffusion control calculated from equation 2, with $n = 4$.

The straight line in figure 2 was calculated assuming $n = 4$ and is an excellent fit to the experimental points for ΔQ from 0 to 25 microcoulombs. Additional adsorption appears to be activation-controlled. This result suggests that ΔQ can be used as a quantitative measure of adsorption. Similar results for a range of potentials are plotted in figure 3, those results suggesting that diffusion control followed by activation control of adsorption occurs over a range of potentials from where the platinum surface is essentially bare (0.7 V) to potentials at which the surface is at least partially covered with oxygen atoms. The ΔQ values are plotted on a linear time scale in figure 4 to show that saturation coverage is achieved early (within 10 s) for $U \leq 0.8$ V, but not fully achieved even at $t = 500$ s at the higher potentials.

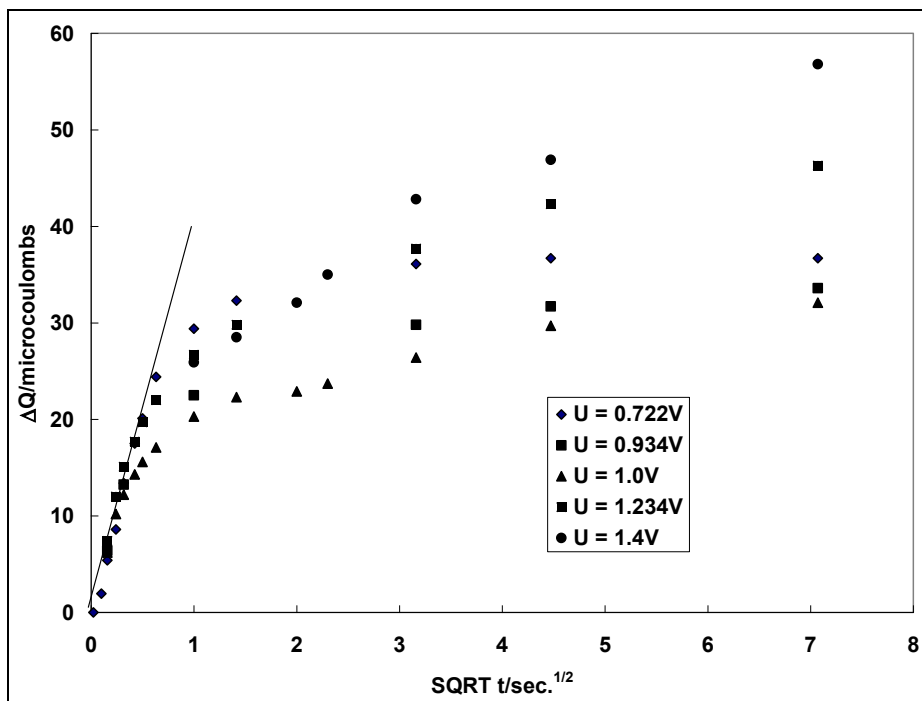


Figure 3. Differential anodic charge corresponding to adsorption of acetate at various potentials from a 10^{-4} M solution of acetic acid in 1N HClO_4 at short adsorption times, $v = 1000$ V/s. The straight line corresponds to diffusion control calculated from equation 2, with $n = 4$.

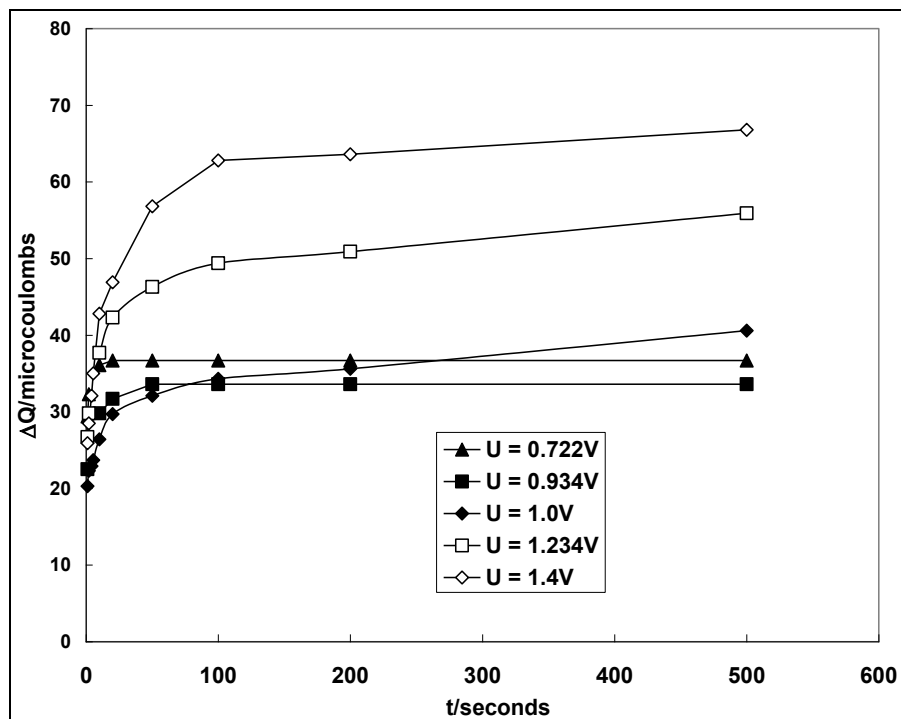


Figure 4. Differential anodic charge corresponding to adsorption of acetate at various potentials from a 10^{-4} M solution of acetic acid in 1N HClO_4

3.3 Determination of Rates of Desorption

The procedure from table 2 with $v = 1000$ V/s and an acetic acid concentration of 10^{-4} M was chosen for these experiments. Figure 5 presents the results of desorption at $U_{\text{des}} = 0.4$ V after 20 s of adsorption at $U_{\text{ads}} = 1.4$ V. The latter potential was chosen as representative of a surface largely covered with adsorbed oxygen and/or a non-stoichiometric oxide. The results lend themselves best to a plot on linear axes, as shown. Unlike the adsorption at this high potential, the desorption to the equilibrium value at 0.4 V is extremely rapid and the question arises as to whether the rate of adsorption is activation influenced or controlled. From equation 2, back diffusion from the bulk of the electrolyte during the anodic scan of approximately 1-ms duration, could only contribute 0.3 microcoulombs to the measured value of ΔQ and is relatively insignificant. However, the desorption may be occurring instantaneously and readsorption from the resulting highly concentrated solution of the acetic acid immediately adjacent to the electrode may account for most or all of the values of ΔQ plotted in figure 5.

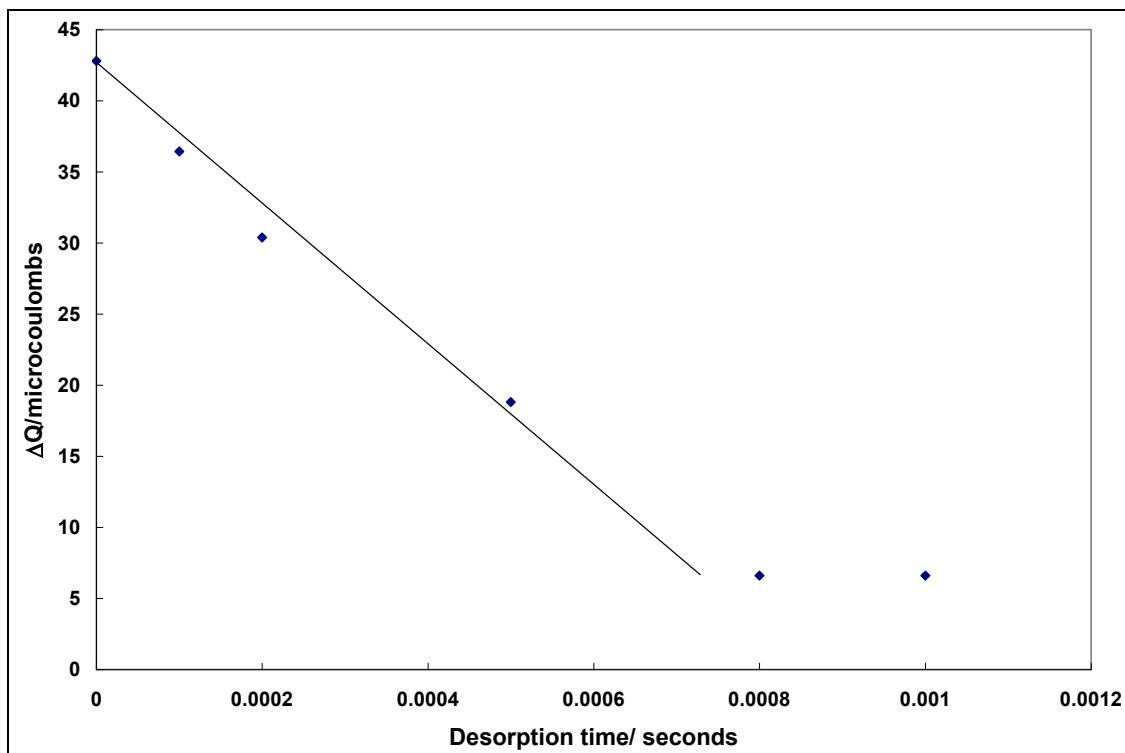


Figure 5. Differential anodic charge when desorbing acetate at $U_{\text{des}} = 0.4$ V after 20 s of adsorption at $U_{\text{ads}} = 1.4$ V, using sequence from table 2. Concentration of acetic acid = 10^{-4} M in 1N HClO_4 .

A second desorption experiment was conducted with $U_{\text{ads}} = 0.73$ V (adsorption for 10 s) and $U_{\text{des}} = 0.33$ V. This value of U_{ads} was chosen as representative of an “oxygen free” surface. The results appear on the semilog plot of figure 6, the suitability of the logarithmic time axis suggesting Temkin kinetics, as can be expected for a heterogeneous surface. The initial and final values of ΔQ on the plot are precisely equal to those measured for saturation coverage when adsorbing using the sequence from table 2, showing that the adsorption in the lower range of potentials is a reversible process. The question arises as to the role of readsorption of acetate from the solution adjacent to the electrode during the anodic scan. The results for the experiment with $U_{\text{ads}} = 1.4$ V (plotted in figure 5) set a lower limit for the possible influence of readsorption from solution during the scan. The desorption from $U_{\text{ads}} = 1.4$ V being an order of magnitude more rapid than that for $U_{\text{ads}} = 0.722$ V suggests that the latter desorption is indeed activation-controlled. The difference probably reflects the stronger affinity of acetate to the highly catalytic bare surface than to the “oxygen” covered surface of platinum and parallels the difference in adsorption rates for the two surface conditions, as already noted in section 3.2.

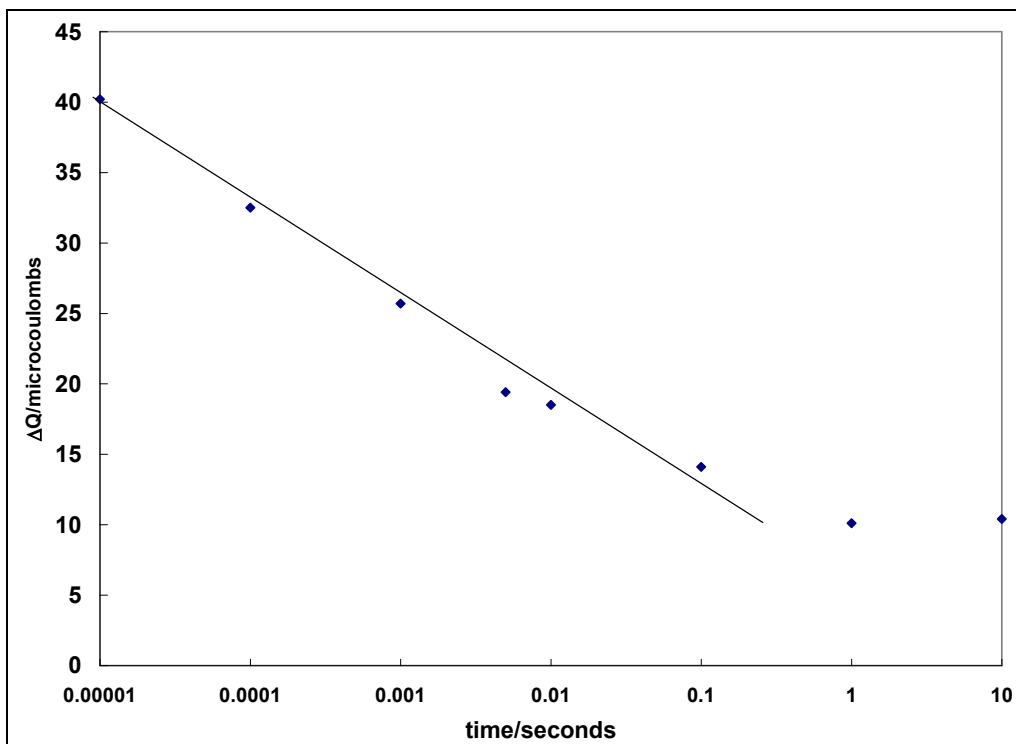


Figure 6. Differential anodic charge when desorbing acetate at $U_{\text{des}} = 0.334$ V after 20 s of adsorption at $U_{\text{ads}} = 0.734$ V, using sequence from table 2. Concentration of acetic acid = 10^{-4} M in 1N HClO_4 .

3.4 Oxidation State of Adsorbed Acetate

A slow (1 mV/s) scan of potentials between 0.4 and 1.6 V for a 10^{-3} M solution of acetic acid in the perchloric acid electrolyte revealed no steady oxidative current corresponding to acetic acid. The current flowing during the adsorption (step 4 of the sequence from table 1) of acetic acid at 0.732 V (figure 2) was monitored and compared with the blank experiment using the perchloric acid electrolyte. The two current-time traces overlapped. Hence, no evidence was found for an oxidative process during adsorption.

3.5 Adsorption Isotherm for Acetate Adsorption

Values of ΔQ were obtained for longer-term adsorption from a 10^{-4} M solution of acetic acid in 1N HClO_4 using the procedure described in section 3.2. Adsorption was measured after 10, 20, 50, 100, 200, 500, and 1000 s; the sampling was discontinued when two successive adsorption intervals yielded the same result. For $U_{\text{ads}} \leq 0.83$, saturation coverage was achieved in only 10 s. For $U_{\text{ads}} = 0.93$, 50 s was required for saturation. For $U_{\text{ads}} \geq 1.0$ V, ΔQ was seen to continue to rise slowly ($\sim 0.01\%/s$ between 500 and 1000 s) even after 1000 s. Adsorptions were not followed for periods longer than 1000 s because of electrolyte purity limitations, and therefore, the values given for surface coverage for the potentials $U_{\text{ads}} \geq 1.0$ are not exactly the saturation/equilibrium values. The experimental values of ΔQ were converted to fractional

surface coverages, Θ , by assuming that full coverage would correspond to the equivalent of a monolayer of oxygen atoms or twice the coulombs for a full monolayer of hydrogen:

$$\Theta = \Delta Q / 2(Q_H)_S, \quad (3)$$

where $(Q_H)_S$ is the number of coulombs required to cathodically deposit a monolayer of hydrogen on the electrode as determined through a cathodic potential scan (12) and F is the Faraday constant. For this electrode, $(Q_H)_S = 117$ microcoulombs. Hence, values of ΔQ were divided by 234 to provide the fractional surface coverages plotted in figure 7.

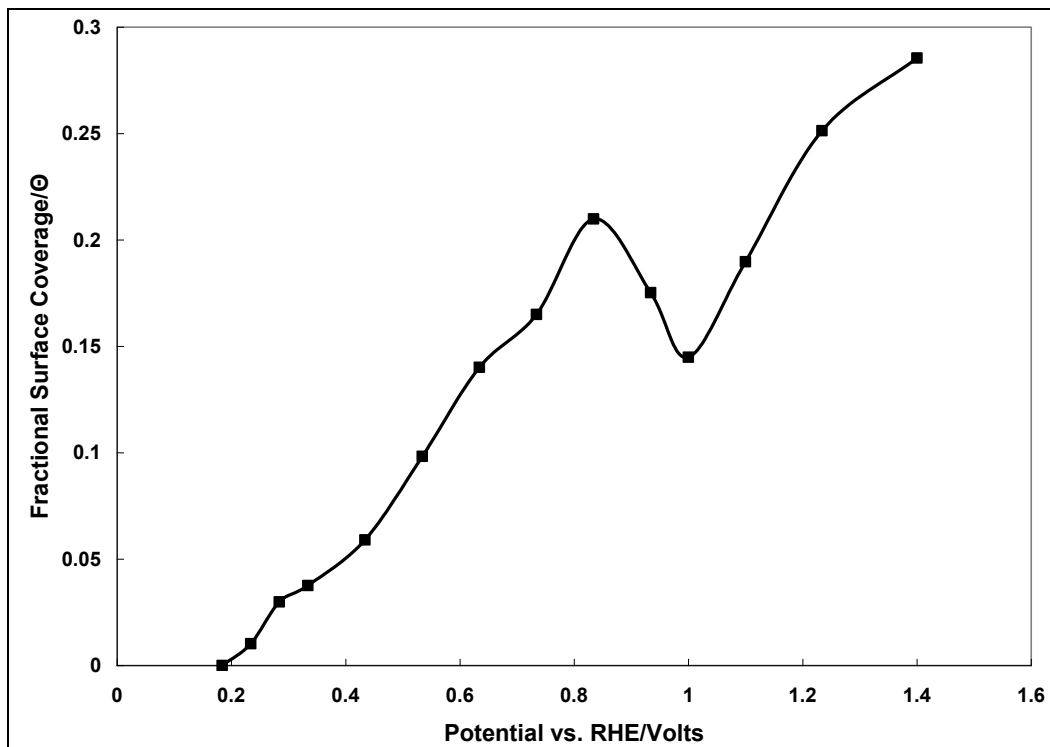


Figure 7. Fractional surface coverage with acetate for a 10^{-4} M solution of acetic acid in 1N $HClO_4$. Values of Θ for potentials of 1.0 V or less are equilibrium values; Θ for potentials greater than 1.0 V show slow increase after 1000 s.

For comparison with other published work, the experimental values of ΔQ can alternatively be converted to “surface excesses.” Assuming that 1 mole of acetate ions obscures four equivalents of hydrogen sites, then the surface excess based on the electrode geometric area, Γ_g , is

$$\Gamma_g = \Delta Q / 4FA_g, \quad (4)$$

where

Γ_g = is the surface excess in moles/cm²

F = the Faraday constant = 96,500 coulombs/equivalent

A_g = the electrode geometric area in square centimeters.

Then

$$\Gamma_g = \Theta (Q_H)_s / 2F. \quad (5)$$

Corrected for the electrode roughness factor 2.1 for this electrode,

$$\Gamma_c = \Theta (Q_H)_s / 4.2F, \quad (6)$$

with $(Q_H)_s = 117 \times 10^{-6}$ coulombs for this electrode.

Some comparison can be made with the results of radioisotope measurements made by Corrigan et al. (6). Those authors used a mechanically polished polycrystalline foil as the electrode and performed their study in a 0.1M HClO₄ solution containing 1 mM of acetic acid. The resulting isotherm resembled that of figure 7. Converting the potentials reported in reference 6 to the Reversible Hydrogen Electrode (RHE) scale, their point of zero charge is apparently 0.14 V, which is in fair agreement with the 0.18 value of figure 7. Their maximum adsorption had a value of 5×10^{-9} M/cm² in exact agreement with the value of Γ_g calculated from figure 7 of this report. The results of figure 7, however, correspond to an order of magnitude lower concentration of acetic acid (i.e., 10^{-4} M vs. 10^{-3} M for the results of reference 6). The results of concentration effects, to be discussed below, predict that our maximum value of Γ_g would be approximately 0.62 M/cm² for the more concentrated solution. The difference compared to the reference 6 results can probably be explained by a corresponding difference in electrode roughness factors for the two electrodes. The roughness factor of the electrode used in the radioisotope experiment was not reported.

The general appearance of the isotherm of figure 7 (approximately linear rise in Θ with increase of potential to a maximum) is typical for anion adsorption. Results using a similar coulometric technique were reported for chloride and phosphate ion adsorption (9). For 10^{-4} M solutions of chloride and phosphate, maximum values of Θ were 0.45 and 0.08, respectively, compared with 0.22 for acetate, according to figure 7.

3.6 Concentration Dependence of Equilibrium Acetate Adsorption

For the lower range of potentials and a wide range of acetic acid concentrations, saturation coverage was observed in 10 s or less. The data points are plotted on figure 8 and conform approximately to parallel semi-logarithmic representations of the results. The logarithmic dependence of Θ on concentration is in accord with the expectations for a heterogeneous surface. Scatter at low concentrations appears reasonable considering the very small values of ΔQ that were measured.

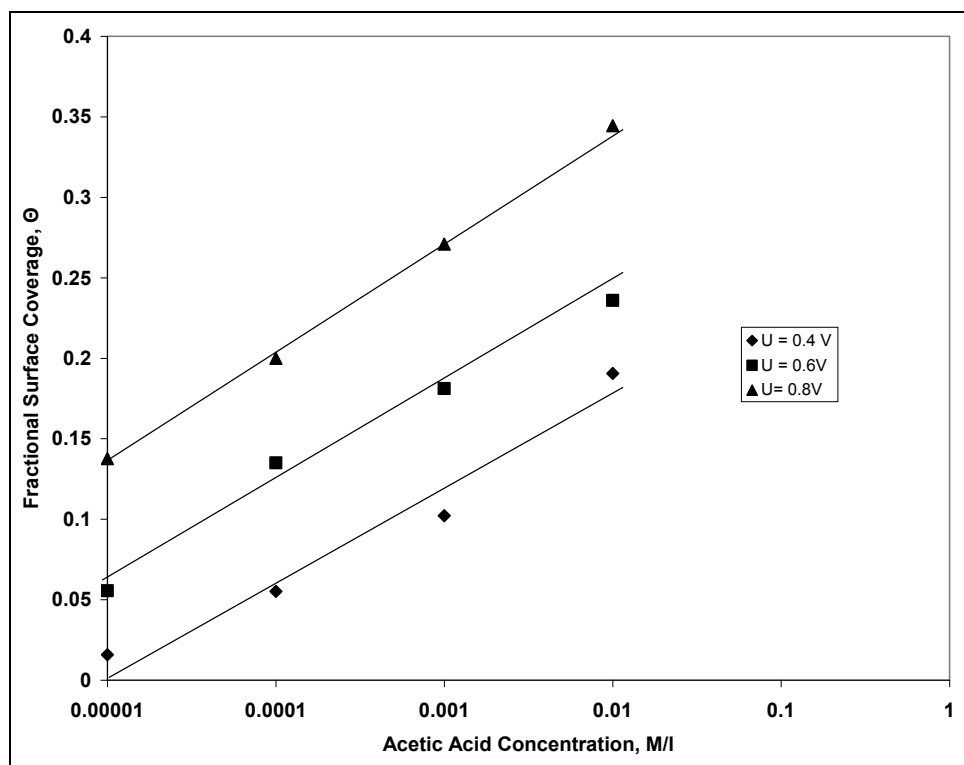


Figure 8. Concentration dependence of fractional surface coverage with acetate ions; 1N HClO₄ supporting electrolyte.

4. Conclusions

The adsorption of acetate ions from dilute solutions of acetic acid in a perchloric acid supporting electrolyte blocks the adsorption of oxygen on a polycrystalline Pt electrode. Until more than half of the steady state fractional surface coverage is exceeded, the time-dependence of oxygen blockage for a freshly activated surface is well predicted by the assumption of semi-infinite linear diffusion with one acetate ion blocking two oxygen adsorption sites. This leads to the conclusion that the charge corresponding to oxygen blockage can serve as a quantitative tool for determination of the fractional coverage of the surface with acetate ions, similar to the situation for chloride and phosphate ions. From oxygen blockage measurements, equilibrium fractional coverages with acetate ion were determined. Rates of acetate desorption could also be determined through the effect on oxygen blockage. The desorptions that were evaluated had “half-lives” in the millisecond and fractional millisecond time range.

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List of Symbols, Abbreviations, and Acronyms

ACS	American Chemical Society
ATR	attenuated total reflectance
CP	chemically pure
FTIR	Fourier transform infrared
HClO ₄	perchloric acid
Pd/H	palladium-hydrogen
Pt	platinum
PTFE	polytetrafluoroethylene
RHE	Reversible Hydrogen Electrode
SCE	saturated calomel electrode

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6 HCS	US ARMY RSRCH LAB RDRL SED E J SHAFFER RDRL SED C C LUNDGREN D CHU R JIANG W BEHL J READ ADELPHI MD 20783-1197
1 HC	CERDEC HDQ ATTN EDWARD PLICHTA 5100 MAGAZINE ROAD ABERDEEN PROVING GROUND, MD 21005

TOTAL: 12 (1 ELEC, 11 HCS)

INTENTIONALLY LEFT BLANK.